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(54) Title: PROCESS FOR THE SYNTHESIS OF CYCLOORGANYLPHOSPHANES AND DI(ALKALI METAL/ALKALINE EARTH METAL) OLIGOPHOSPHANEDIIDES

(57) Abstract: The invention relates to a process for the preparation of cycloorganylphosphanes of formula  $1(R^1P)_n$  by reaction of dihalo(organyl)phosphanes of formula  $R^1PHal_2$  with: a) activated zinc in an organic solvent, or with: b) an alkali metal or alkaline earth metal in a non-polar organic solvent in the presence of an activator, wherein  $R^1$  is  $C_1$ - $C_{12}$ alkyl;  $C_3$ - $C_{12}$  cycloalkyl, aryl or heteroaryl, Hal is F, Cl, Br or I, and n is a number from 3 to 20. The invention relates also to novel di(alkali metal/alkaline earth metal) oligophosphanediides and to the use thereof in the preparation of organophosphorus compounds.

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## INTERNATIONAL SEARCH REPORT

Internat. application No

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07F9/6564

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PASS F ET AL: "ORGANISCHE VERBINDUNGEN DES PHOSPHORS. I. MITT. UEBER DIE DARSTELLUNG PRIMAERER PHOSPHINE DURCH REDUKTIVE METHODEN" MONATSHEFTE FUR CHEMIE, SPRINGER VERLAG. WIEN, AT, vol. 90, 1959, pages 148-156, XP009005184 ISSN: 0026-9247 cited in the application	2, 4, 6
X	page 155, paragraphs 1,2 ----- -/--	1, 3, 5

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

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\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HINKE A ET AL: "ZUR KENNTNIS DER ORGANOPHOSPHORVERBINDUNGEN, XXII 1,2-DIARYL-1,2-DIBROMDIPHOSPHANE ON ORGANOPHOSPHORUS COMPOUNDS, XXII 1,2-DIARYL-1,2-DIBROMODIPHOSPHANES" CHEMISCHE BERICHTE, VERLAG CHEMIE GMBH. WEINHEIM, DE, vol. 116, no. 5, September 1983 (1983-09), pages 3003-3010, XP009005658 ISSN: 0009-2940 cited in the application	2,4,6
X	G1. 2a page 3004	1,3,5
A	--- HENDERSON W A ET AL: "Some Apsects of THE CHEMISTRY OF Cyclopolyphosphines" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 85, 1963, pages 2462-2466, XP002233272 ISSN: 0002-7863 cited in the application	2,4,6
X	page 2466, left-hand column, paragraphs 1,2	1,3,5
A	--- SCHISLER A ET AL: "SYNTHESIS, PROPERTIES, STRUCTURE AND REACTIVITY OF SODIUM 2,3,4,5-TETRA-TERT-BUTYLCYCLOPENTAPHOSPHAN IDE" PHOSPHORUS, SULFUR AND SILICON AND THE RELATED ELEMENTS, GORDON AND BREACH SCIENCE PUBLISHERS, AMSTERDAM, GB, vol. 177, no. 6/7, 2002, pages 1447-1450, XP009005162 ISSN: 1042-6507 the whole document	1-9
A	--- BAUDLER M: "CHAIN AND RING PHOSPHORUS COMPOUNDS-ANALOGIES BETWEEN PHOSPHORUS AND CARBON CHEMISTRY" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, VERLAG CHEMIE. WEINHEIM, DE, vol. 21, 1982, pages 492-512, XP009005878 ISSN: 0570-0833 the whole document	1-9
A	--- BLOOMFIELD P R ET AL: "DIRECT PREPARATION OF PHENYLPHOSPHINE DILITHIUM" JOURNAL OF APPLIED CHEMISTRY, SOCIETY OF CHEMICAL INDUSTRY. LONDON, GB, 25 April 1959 (1959-04-25), pages 541-543, XP009005175 the whole document	1,3-5
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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>KUHN N ET AL:  "DICHLORO(TETRAMETHYLPYRROLYL)PHOSPHANE,  BIS(TETRAMETHYLPYRROLYL)CHLOR OPHOSPHANE,  TRIS(TETRAMETHYLPYRROLYL)PHOSPHANE,  1,1,2,2,-TETRAKIS(TETRAMETHYLPYRROLYL)DIPH  OSPHANE,  TETRAKIS(TETRAMETHYLPYRROLYL)CYCLOTETRAPHO  SPHANE - (C4ME4N)PCL2, (C4ME4N)2PCL,  (C4ME4N"  SYNTHETIC METHODS OF ORGANOMETALLIC AND  INORGANIC CHEMISTRY, XX, XX,  vol. 4, 1997, pages 76-79, XP001122390  the whole document</p> <p>---</p>	1,3,4
A	<p>JUTZI P ET AL:  "PENTAMETHYLCYCLOPENTADIENYL-SUBSTITUTED  PHOSPHANES, DIPHOSPHANES, CYCLOPHOSPHANES,  1,2-DIPHOSPHASELENIRANES, DIPHOSPHENES-  CP*PX2(X = CL, BR, H), CYCLOACP*PÜ3,  CP*-P-SE-P-CP*, (CP*)(I)P-P(I)(CP*),  CP*-P=PCP*, AR*-P=P-CP*"  SYNTHETIC METHODS OF ORGANOMETALLIC AND  INORGANIC CHEMISTRY, XX, XX,  vol. 3, 1996, pages 113-118, XP001122389  the whole document</p> <p>---</p>	1,3,4
A	<p>BAUDLER M ET AL: "MONOCYCLIC AND  POLYCYCLIC PHOSPHANES"  CHEMICAL REVIEWS, AMERICAN CHEMICAL  SOCIETY. EASTON, US,  vol. 93, 1983, pages 1623-1667,  XP002233273  ISSN: 0009-2665  the whole document</p> <p>-----</p>	1-9

# INTERNATIONAL SEARCH REPORT

Int'l application No.  
PCT/EP 03/50873

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 2 completely; 1, 5 partially

Claims 1, 2, 5 concern a process for preparing a cylcoorganylphosphane by reaction of dihalo(organyl)phosphane with activated zinc in an organic solvent.

1.1. Claims: 3, 4, 6-9 completely; 1, 5 partially

Claims 1, 3-9 concern a process for preparing a cylcoorganylphosphane by reaction of dihalo(organyl)phosphane with an alkali metal or an alkaline earth metal in a non polar organic solvent in the presence of an activator, a di(alkali metal/alkaline earth metal) oligophosphanediide, the preparation and the use thereof.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.